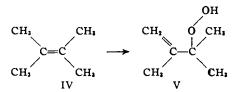
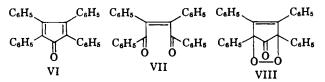


The reaction of 2,3-dimethylbutene-2 (IV) gives 2,3dimethyl-3-hydroperoxybutene-1 (V), 63%, b.p. 54° (9 mm.),  $n^{24.5}$ D 1.4408; the infrared and n.m.r. spectra are identical with those of the product of the photosensitized autoxidation (formed in 54% yield; lit.<sup>14</sup>: 82%, b.p. 55° (12 mm.),  $n^{29}$ D 1.4428).



Tetraphenylcyclopentadienone. (VI) gives *cis*-dibenzoylstilbene (VII, 50%, m.p. 215.9–216.3°, infrared spectrum identical with that reported<sup>16</sup>). The photosensitized autoxidation gave VII in 65%yield.<sup>16</sup> The peroxide VIII is presumably intermediate.



Cyclohexadiene-1,3 (IX) gives 5,6-dioxabicyclo-[2.2.2]octene-2 ("norascaridol," X, 20%), with infrared and n m r. spectra identical with those of a sample prepared by the photosensitized autoxidation (35%yield; lit.<sup>17</sup> 21%).



Preliminary indications are that rubrene and other aromatic hydrocarbons also form peroxides analogous to those formed photochemically.<sup>18</sup>

Sample Procedure.—To a solution of 5.05 g. (60 mmoles) of 2,3-dimethylbutene-2 (IV) in 300 ml. of methanol was added 19.2 ml. of 30% H<sub>2</sub>O<sub>2</sub> [180 mmoles). The solution was stirred at  $10^{\circ}$ , and 145.5 ml. of 1.03 *M* NaOCl solution (150 mequiv.) was added in the course of 90 min. The solution was diluted with water and extracted with ether. Ether was distilled from the dried extracts through a column to prevent loss of the volatile product. The residue was

(15) D. R. Berger and R. K. Summerbell, J. Org. Chem., 24, 1881 (1959).
(16) C. F. Wilcox, Jr., and M. P. Stevens, J. Am. Chem. Soc., 84, 1258 (1962); G. O. Schenck, Z. Elektrochem., 56, 855 (1952).

(17) G. O. Schenck and W. Willmund, reported by R. Criegee in Houben-Weyi, "Meth-den der Organischen Chemie," Vol. VIII, 4th Ed., E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1952, p. 16. The yields referred to above are of distilled but unrecrystallized material.

(18) Corey has recently found that externally generated singlet O: is capable of oxidizing aromatic hydrocarbons: E. J. Corey and W. C. Taylor, J. Am. Chem. Soc., **86**, 3881 (1964).

distilled, giving 4.39 g. (37.8 mmoles, 63%) of V, with the physical constants described above.

The new reaction parallels the photosensitized autoxidations in every case so far studied; it appears to be a general and practical synthetic method for oxidization of olefins which give high quantum yields in the photosensitized autoxidation (for example, s-cis dienes, furans, and tri- and tetrasubstituted olefins). The products (when they are peroxides) are, of course, readily reduced to the corresponding alcohols. Where the parallel photosensitized autoxidation goes in low quantum yield, it is likely that the peroxide-hypochlorite reaction will be less useful, because of the large quantities of reagents which would be required: this suggestion is supported by preliminary studies. The quantities of oxidant are best adjusted so that nearly 1 mole of oxygen is actually taken up; the oxygen which evolves from the solution (small amounts with good acceptors such as dimethylfuran) is collected in a gas buret so that this loss can be compensated by further addition of reagents. The use of excess  $H_2O_2$ appears to be of value in preventing further oxidation of the products.

The reaction is being extended to other acceptors and to other systems potentially capable of yielding singlet oxygen.

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## Singlet Oxygen. A Probable Intermediate in Photosensitized Autoxidations<sup>1</sup>

Sir:

Several mechanisms have been suggested for the dyephotosensitized autoxidations of dienes and olefins, studied in detail by Schenck,<sup>2</sup> and the analogous photooxidations of aromatic hydrocarbons, studied by many workers, particularly by Bowen.<sup>3</sup> Of these mechanisms, all but two have been ruled out by careful kinetic studies and by other criteria such as product or energy considerations. The two mechanisms which are consistent with the kinetics differ only in steps 3 and 4 (see below). In mechanism a (originally proposed by

Sens 
$$\xrightarrow{h_{\nu}}$$
 <sup>1</sup>Sens (1)

 $^{1}\text{Sens} \longrightarrow ^{3}\text{Sens}$  (2)

$$^{3}\text{Sens} + ^{3}\text{O}_{2} \longrightarrow \text{Sens} - \text{O} - \text{O} \cdot$$
 (3a)

$$Sens-O-O \cdot + A \longrightarrow AO_2 + Sens$$
(4a)

$$\operatorname{Sens} + {}^{3}\operatorname{O}_{2} \longrightarrow \operatorname{Sens} + {}^{1}\operatorname{O}_{2}$$
(3b)

$$^{1}O_{2} + A \longrightarrow AO_{2}$$
 (4b)

Schönberg<sup>4</sup>), the postulated reactive intermediate (an adduct ( $\cdot$ SensOO $\cdot$ ) of sensitizer (Sens) and oxygen) reacts with acceptor (A) to form the product peroxide (AO<sub>2</sub>). Mechanism b was originally proposed by

<sup>(14)</sup> G. O. Schenck and K. Schulte-Elte, Ann., 618, 185 (1958).

<sup>(1)</sup> Supported by N.S.F. Grant G-25086; we are pleased to acknowledge heipful discussions with Professor K. D. Bayes,

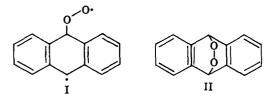
 <sup>(2) (</sup>a) G. O. Schunck, Angew. Chem., 69, 579 (1957); (b) Naturwiss.,
 35, 28 (1948); (c) ibid. 40, 205, 229 (1953); (d) G. O. Schenck and E. Koch,
 Z. Elektrochem., 64, 170 (1960)

<sup>(3)</sup> E. J. Bowen in "Advances in Photochemistry," Vol. 1, W. A. Noyes, G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 23, and references therein cited.

<sup>(4)</sup> A. Schönberg, Ann., 518, 299 (1935).

The evidence which supports mechanism a is as follows. (1) Gaffron found that with one sensitizer, at least, light of 8200 Å. is effective. Since this wave length is of insufficient energy to excite the  ${}^{1}\Sigma_{g}^{+}$  state of O<sub>2</sub>, Gaffron concluded that singlet oxygen could not be intermediate.<sup>6</sup> Kautsky, however, pointed out that there was ample energy in Gaffron's system to excite oxygen to the lower-lying  ${}^{1}\Delta_{g}$  state.<sup>5c</sup> (2) Livingston's kinetic studies indicate that the active intermediate has somewhat different kinetic behavior when formed with anthracene or with diphenylanthracene as sensitizer.<sup>7</sup> The rates were measured indirectly, and with a fairly high probable error, making this conclusion somewhat questionable. In other cases, Schenck has found that the rate of disappearance of the active intermediate does not depend on sensitizer.2d

Until now, the singlet oxygen mechanism has been generally disregarded despite the following observations. (1) Kautsky observed that reaction occurs even when sensitizer and acceptor are adsorbed on separate granules of silica gel, which would indicate that a reactive intermediate is formed which is capable of diffusion under vacuum.<sup>5a,b</sup> Similar phenomena were noted by Rosenberg and Shombert.<sup>8</sup> No satisfactory explanation of these observations in terms of mechanism a has yet been made. (2) The "moloxide" would have to have an unexpected property; for example, in the reaction with anthracene, which is both sensitizer and acceptor, the kinetics require that the intermediate (which, if it is a moloxide, is presumably of structure I) cannot collapse to product II itself, but must transfer oxygen to a second anthracene molecule.<sup>3,9</sup>



Since singlet oxygen has now been shown to be effective in carrying out reactions identical with the photosensitized autoxidations,<sup>10</sup> the weight of the evidence favors the intermediacy of singlet oxygen. Further experiments are in progress.

(5) (a) H. Kautsky and H. de Bruijn, Naturwiss., 19, 1043 (1931); (b) H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister, Ber. deut. chem. Ges., 66, 1588 (1933); (c) H. Kautsky, Biochem. Z., 291, 271 (1937).

(6) H. Gaffron, ibid., 287, 130 (1936), and references cited therein.

(7) R. Livingston and V. Subba Rao, J. Phys. Chem., 63, 794 (1959).
(8) J. L. Rosenberg and D. J. Shombert, J. Am. Chem. Soc., 82, 3527 (1960).

(9) G. O. Schenck, Naturwiss., 41, 452 (1954).

(10) (a) C. S. Foote and S. Wexler, J. Am. Chem. Soc., 86, 3879 (1964);
(b) E. J. Corey and W. C. Taylor, *ibid.*, 86, 3881 (1964).

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## A Study of the Peroxidation of Organic Compounds by Externally Generated Singlet Oxygen Molecules

Sir:

The existence of two low-lying metastable singlet states of diatomic oxygen ( ${}^{1}\Delta_{g}$  and  ${}^{1}\Sigma_{g}$  which are 0.977

and 1.63 e.v. above the ground state)<sup>1</sup> and the "forbiddenness" of radiative return to the ground state suggested the possibility that singlet  $O_2$  might be a useful and selective reagent in organic chemistry. We were further interested in this case as a result of our previous experience with another highly reactive small molecule, diimide<sup>2</sup> (N<sub>2</sub>H<sub>2</sub>), and because of the possible importance of metastable  $O_2$  in photosensitized peroxidations.<sup>3,4</sup> It seemed to us that the  $O_2$  molecule, raised above its ground state by *ca.* 22.5 or 37.5 kcal./ mole and converted to a singlet state (removing spinconservation difficulties in forming singlet products from reactants of singlet multiplicity), could reasonably be expected to afford the same reactions as observed in sensitized photooxidation.<sup>3</sup>

Our initial studies have been conducted using gaseous oxygen subjected to electrodeless discharge at 6.7 Mc., a method for producing singlet O<sub>2</sub> first described by Foner and Hudson.<sup>6</sup> The radiofrequency unit was a T21/ARC-5 U. S. surplus aircraft transmitter (modified to permit resonant coupling to the discharge tube) with the output leads attached (by platinum wire) to two aluminum foil bands (2 cm. apart) fitted around quartz tubing (12-mm. o.d.). Oxygen was passed through the quartz tube at ca. 20 mm. with the discharge operating to produce a definite glow in the tube between the aluminum terminals, and the emerging gas was bubbled into a solution of the reactant (usually stirred). The reactor was located downstream from the discharge zone by 20-30 cm.; the exact distance did not appear to be a critical variable, however. A water aspirator was employed at the end of the system to pull gas through. The vessel containing the organic reactant was shielded from light by a covering of aluminum foil.

Using this apparatus and bromobenzene as solvent at 0°, anthracene, 9,10-diphenylanthracene, and 9,10dimethylanthracene were cleanly converted to the corresponding 9,10-endoperoxides, identical with authentic samples prepared by the photooxidation route. No other product could be detected. In control experiments in the same apparatus, under the same conditions but with the radiofrequency unit and discharge off, no more than trace quantities of peroxide were formed (analysis by chromatography). Therefore, the zero level of the  ${}^{3}\Sigma_{g}$  ground state of O<sub>2</sub> is not responsible for endoperoxide formation. It also seems improbable that vibrationally excited  ${}^{3}\Sigma_{g}$  molecules could persist long enough to effect oxidation in solution. Ozone and monatomic oxygen can also be excluded since these would lead to other types of products.<sup>6-8</sup> The species

(1) See G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., New York, N. Y., p. 560, for example.

(2) E. J. Corey and W. L. Mock, J. Am. Chem. Soc., 84, 865 (1962), and previous papers; see also S. Hunig, H. Muller, and W. Thier, Tetrahedron Letters, No. 11, 353 (1961); E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, J. Am. Chem. Soc., 83, 3725 (1961).

(3) For a recent review see G. O. Schenck, Angew. Chem., 69, 579 (1957).
(4) This possibility appears to have been suggested first by H. Kautsky and H. deBruijn, Naturwiss., 19, 1043 (1931).

(5) S. N. Foner and R. L. Hudson, J. Chem. Phys., 25, 601 (1956); 23, 1974 (1955).

(6) R. J. Cvetanovic, "Advances in Photochemistry," Vol. 1, 1nterscience Publishers, Inc., New York, N. Y., 1963, p. 115.

(7) R. E. Erickson, P. S. Bailey, and J. C. Davis, Jr., Tetrahedron, 18, 389 (1962).

 <sup>(8)</sup> P. S. Bailey, Chem. Rev., 58, 926 (1958); P. S. Bailey, P. Kolsaker,
 B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, J. Org. Chem., 29, 1400 (1964).